Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

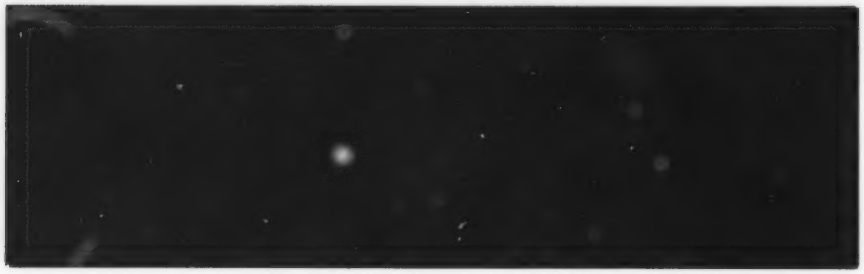
CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Coal Research Laboratories

Laboratoires de recherche sur le charbon



Canada

A FIXED POINT CALIBRATION CURVE GENERATOR FOR GAS ANALYSIS

D.J. Kennedy

Division Report CRL 89-58(TR)
June 1989

MICROMEDIA

19AP

90-01323/

A FIXED POINT CALIBRATION CURVE GENERATOR FOR GAS ANALYSIS

by

D.J. Kennedy*

ABSTRACT

This report describes a gas mixing device developed at the Cape Breton Coal Research Laboratory. This instrument is capable of quickly and accurately preparing a series of 32 standard mixtures by dynamically blending primary gas standards with zero air. Sample injection techniques for gas chromatography are also discussed.

---

*Analytical Scientist, Cape Breton Coal Research Laboratory, CRL, CANMET, Energy, Mines and Resources Canada, Sydney.

D.J. Kennedy

RÉSUMÉ

Le présent rapport contient une description d'un appareil de mélange de gaz mis au point au Laboratoire de recherche sur le charbon du Cap-Breton. Cet instrument sert à préparer rapidement et avec précision une série de 32 mélanges étalons composés d'étalons gazeux primaires avec de l'air ultra pur. Des techniques d'injection d'échantillons en chromatographie en phase gazeuse sont également présentées.

CONTENTS

	Page
ABSTRACT	i
RESUME	iii
INTRODUCTION	1
INSTRUMENT DESCRIPTION	1
Block Diagram	1
Zero Air flow Control	5
Standard Flow Control	5
Standard Selection	7
Manual Switching Valve	7
Mixing Chamber	7
Flow Measurement	10
Tubing Tips	10
Sample Injection	10
CONCLUSIONS	12
REFERENCES	12
APPENDIX A	13

TABLES

No.		Page
1.	Mixing a 1 ppm SF_6 in air standard with zero air. Zero air flow fixed at 250 ccm	3
2.	Capillary tubing installed on 16-position valve	8

FIGURES

1.	Double decade diluter showing the air actuated valve controllers	2
2.	Block diagram of double decade diluter	4
3.	Flowpath for Valco CST16P valve	6
4.	Flowpath for Valco C4P valve	6
5.	Double decade diluter showing an overview of the plumbing	9
6.	Flushing a gas sampling valve	11

INTRODUCTION

This report describes a gas blending device capable of preparing a series of gas standards over a range of two orders of magnitude. The unit is called the double decade diluter. This instrument was developed at the Cape Breton Coal Research Laboratory to calibrate gas chromatographs configured for tracer gas analysis. The tracer gas samples normally contain from 5 to 500 parts per billion (ppb) sulfur hexafluoride in mine air. Since the chromatographic detector response to sulfur hexafluoride is not linear (1), a device was needed to quickly and accurately prepare standard mixtures of SF_6 in air. Figure 1 is a photograph of the double decade diluter showing the air actuated valve controllers.

INSTRUMENT DESCRIPTION

The diluter mixes one of two standard mixtures of SF_6 in air with zero air[1]. The zero air flow is set at 250 cubic centimeters per minute (ccm) and the standard flow can be varied from 13.2 to 250 ccm in 15 fixed steps. A series of 16 standards from 50 to 500 ppb SF_6 in air can be prepared from a 1 part per million (1000 ppb) mixture of SF_6 in air. Using a 100 ppb mixture of SF_6 in air as the second standard, an additional 16 mixtures from 5 to 50 ppb SF_6 in air can be prepared. Table 1 shows flowrates selected to allow for 5 to 6 points on a calibration graph with each doubling in concentration.

BLOCK DIAGRAM

Figure 2 shows a block diagram of the diluter. The inlet gas supplies are stored in three compressed gas cylinders. The author recommends using double stage regulators for supply pressure reduction. An inlet pressure of 69 to 138 kPa (10 to 20 psi) should be provided for each of the two standards and the zero air.

---

[1]For preparing SF_6 standards in the range of 5 ppb to 500 ppb, we can define zero air as pure compressed air containing less than 10 parts per trillion SF_6. The zero air cylinder should be analyzed for SF_6 content before use.

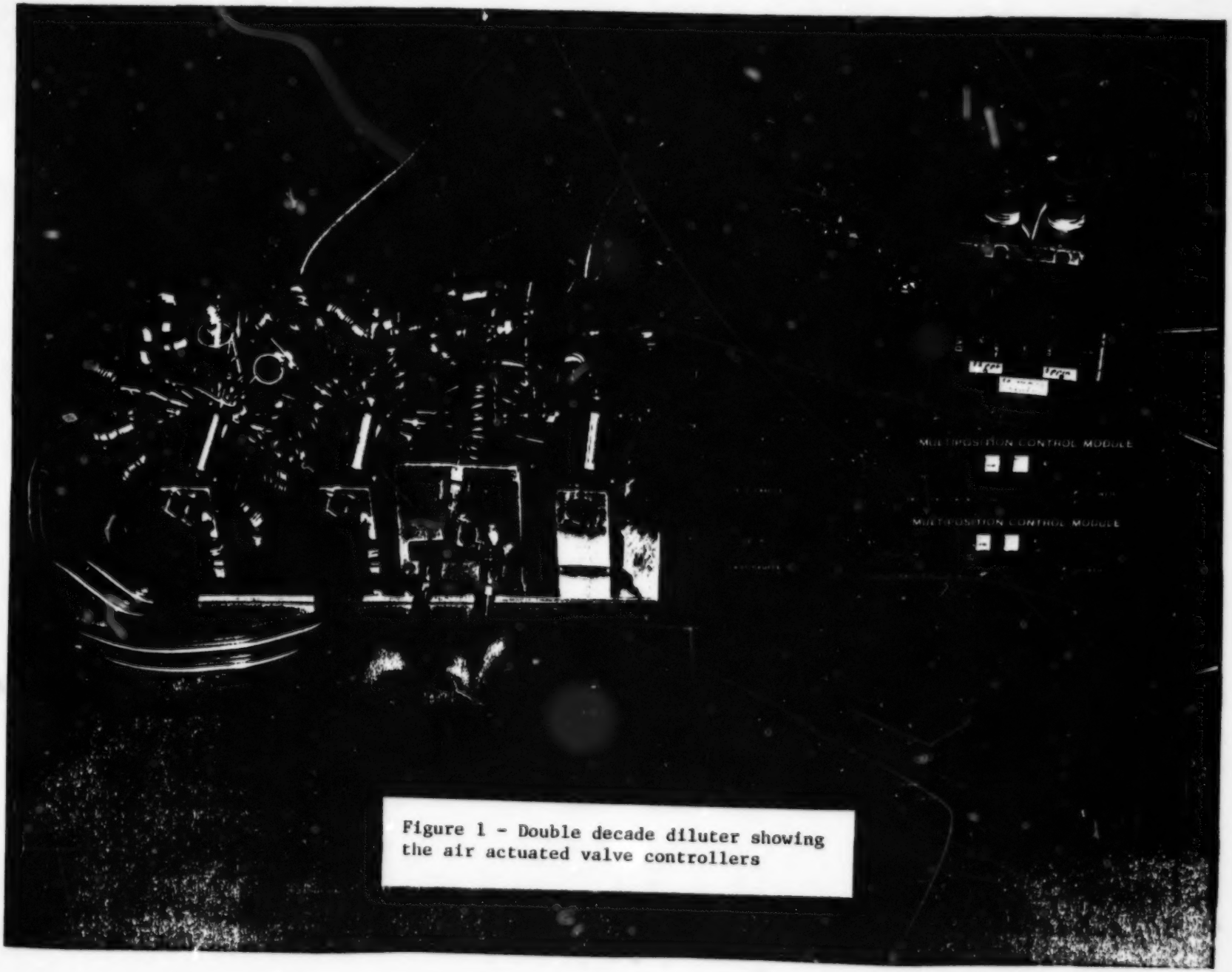


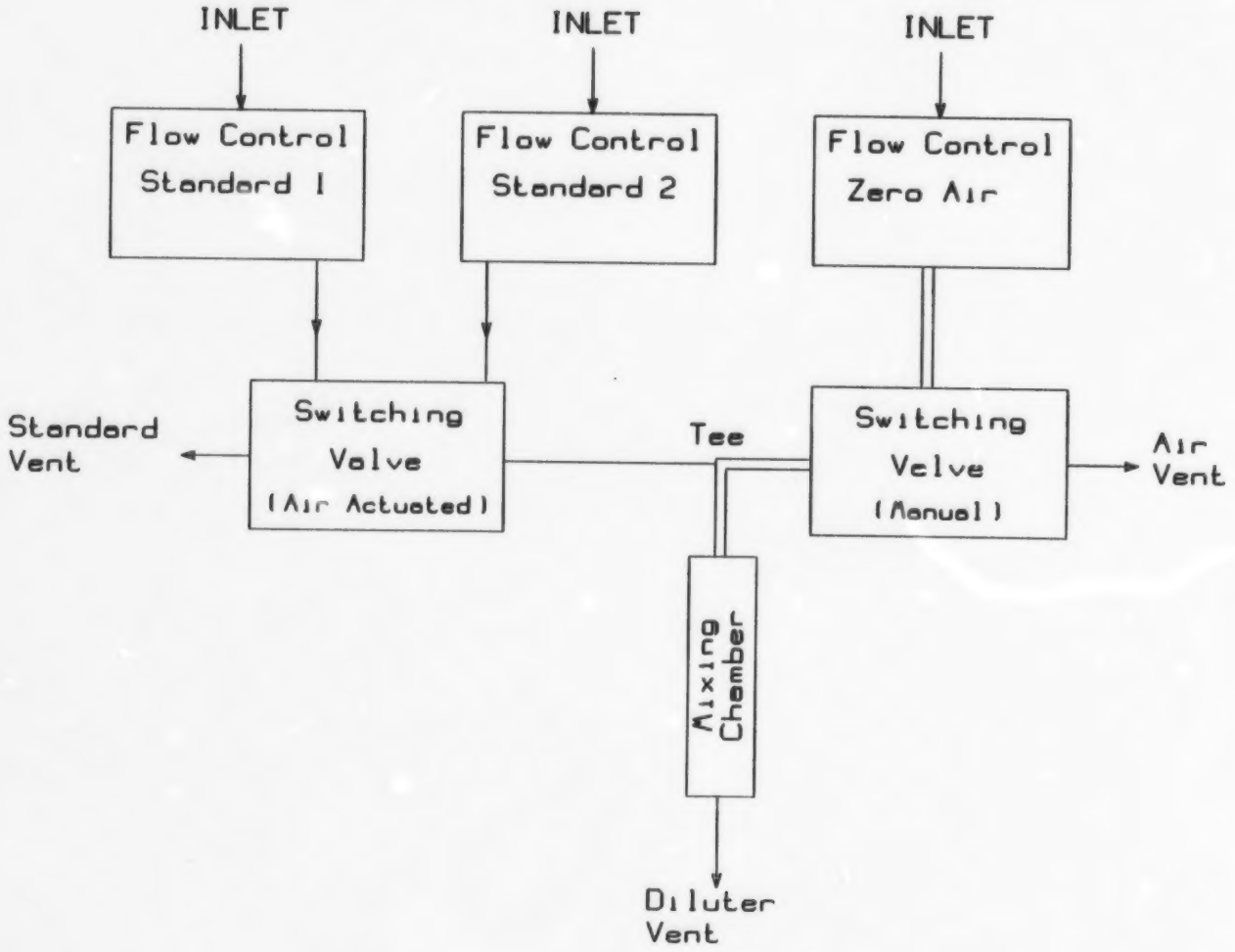
Figure 1 - Double decade diluter showing the air actuated valve controllers

TABLE 1 - Mixing a 1 ppm SF6 in air standard with zero air.

Zero air flow fixed at 250 ccm

STANDARD FLOW (ccm)	DILUTER MIXTURE (ppb)
13.16	50
15.96	60
18.82	70
21.74	80
24.73	90
27.78	100
35.7	125
44.12	150
53.03	175
62.5	200
83.3	250
107.1	300
134.6	350
166.7	400
204.5	450
250	500

Figure 2 - Block Diagram of Double Decade Diluter



ZERO AIR FLOW CONTROL

The zero air supply is delivered to the mixing chamber at a fixed flowrate of approximately 250 ccm. A differential pressure regulator (available from ITT Conoflow Regulators and Controls, St. George, SC, U.S.A.) is used to reduce the inlet pressure to 22 kPa (3.2 psi). A length of stainless steel (SS) capillary tubing is used as a flow restrictor across the differential pressure regulator. About 30 cm of 0.5 mm (0.02") I.D. tubing provides the restriction. The author has used this method for tracer gas release systems and has found that it provides a very stable flowrate. Less than 0.25% variation was experienced in underground coal mines where fluctuations in ambient temperature are usually negligible over short-term periods (4 to 6 hours). Experience in the laboratory will tell whether fluctuations in room temperature cause drifting of the diluter output flows. If these are found to be significant, the unit will have to be placed in a constant temperature enclosure.

STANDARD FLOW CONTROL

Standard flow control is achieved in a manner similar to zero air control. A fixed restrictor and a differential pressure regulator are used on each standard gas supply. Instead of a single fixed restrictor, 16 fixed restrictors are provided for each differential pressure regulator. Since two standard flow controllers are identical, the following discussion will pertain to a single standard flow controller.

A Valco type CST16P valve is placed across a differential pressure regulator. Figure 3 shows the flowpath for this valve (2). Although the valve diagram shows only 6 loops, the valve used on the diluter has 16 loops. The inlet and outlet connects one of the 16 restrictors across the differential pressure regulator. As the valve is rotated, each of the restrictors is placed in sequence across the differential pressure regulator. The other restrictors are isolated from the standard stream.

The restrictor selection valve may be operated manually or by means of either electric or compressed air actuators. The double decade diluter uses compressed air actuators since these were available at the time of construction. The electric or air actuators may be computer controlled. This provides a way to automate the calibration procedure.

The 16 restrictors are made from various lengths of 1.6 mm (1/16") stainless steel capillary tubing with an internal diameter of either 0.25 mm

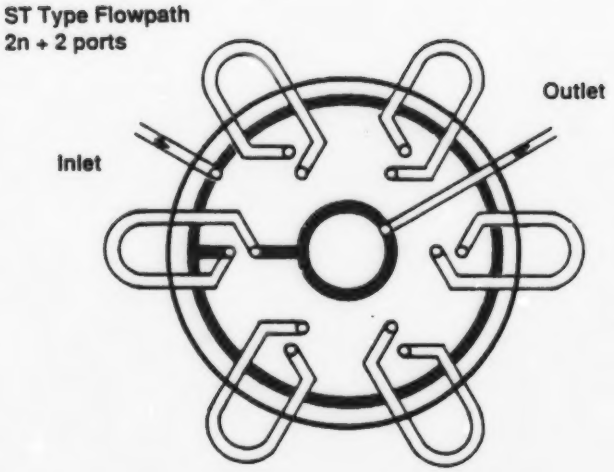


Figure 3 - Flowpath for Valco CST16P valve

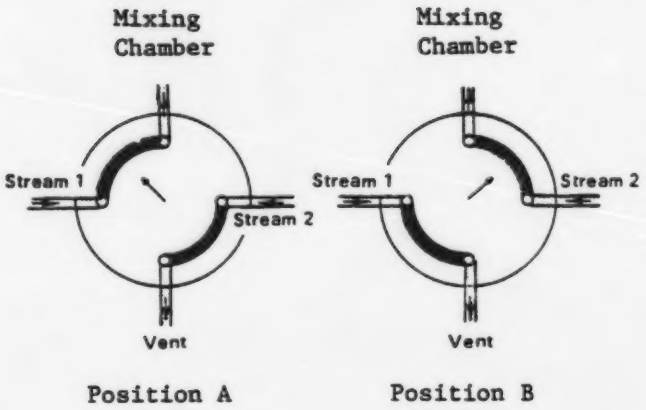


Figure 4 - Flowpath for Valco C4P valve

(0.01") or 0.5 mm (0.02"). Table 2 shows the tubing lengths used and the flowrates achieved. These should be used only as guides if the reader decides to build a diluter. Identical lengths of capillary tubing sometimes give different flow restrictions due to variations in the bore. It should also be noted that coiling the tubing will normally increase the flow restriction. The flowrates in Table 2 are for lengths of tubing coiled (using a 16 mm diameter rod) and installed on the 16-position valve.

STANDARD SELECTION

The air actuated switching valve on the block diagram is a 2-position Valco Model C4P. This valve is configured to allow standard 1 to flow to the mixing chamber while standard 2 is directed to a vent port (position A). Switching this valve to position B directs standard 2 to the mixing chamber and standard 1 to the vent port. Figure 4 shows the flowpath for this valve (3).

MANUAL SWITCHING VALVE

The zero air stream passes through a manual switching valve before arriving at the mixing chamber. This valve allows the zero air stream to be directed either to the mixing chamber or to a vent port. When the zero air stream is directed to vent, all three gas streams may be measured independently. The valve used is a Whitey Ball Valve Model SS-41XS2.

MIXING CHAMBER

A 1.6 mm (1/16") diameter hole was drilled in a Swagelok union elbow (Catalogue Number SS-200-9). A short length of 0.5 mm (0.02") I.D. by 1.6 mm (1/16") O.D. SS capillary tubing was inserted and brazed onto the union elbow. The other end of this 1.6 mm (1/16") tubing was connected to the air actuated switching valve. One side of the union elbow was connected with 3.2 mm (1/8") SS tubing to the manual switching valve. The zero air and the standard flows meet at an angle of 180 degrees in the union elbow. Flowrates and tubing internal diameters have been chosen for turbulent mixing within the chamber. A 61 cm length of 3.2 mm (1/8") SS tubing takes the gas stream from the union elbow to the diluter vent. This 61 cm length of tubing was coiled around a 16 mm diameter rod and shaped to fit the instrument as shown in Figure 5.

TABLE 2 - Capillary tubing installed on 16-position valve

VALVE POSITION	TUBING ID	TUBING LENGTH (cm)	FLOW RATE (ccm)*
1	0.25 mm (0.01")	73.0	12.8
2	0.25 mm (0.01")	57.0	16.1
3	0.25 mm (0.01")	48.5	18.7
4	0.25 mm (0.01")	44.0	21.8
5	0.25 mm (0.01")	38.5	24.2
6	0.25 mm (0.01")	31.7	28.5
7	0.25 mm (0.01")	25.0	35.4
8	0.25 mm (0.01")	20.0	43.8
9	0.25 mm (0.01")	14.9	52.7
10	0.25 mm (0.01")	12.7	62.7
11	0.25 mm (0.01")	8.0	85.6
12	0.5 mm (0.02")	100.0	103.9
13	0.5 mm (0.02")	71.5	134.4
14	0.5 mm (0.02")	55.0	165.2
15	0.5 mm (0.02")	39.7	202.5
16	0.5 mm (0.02")	30.0	249.4

* @ 25.3 deg.C and 771 mm Hg

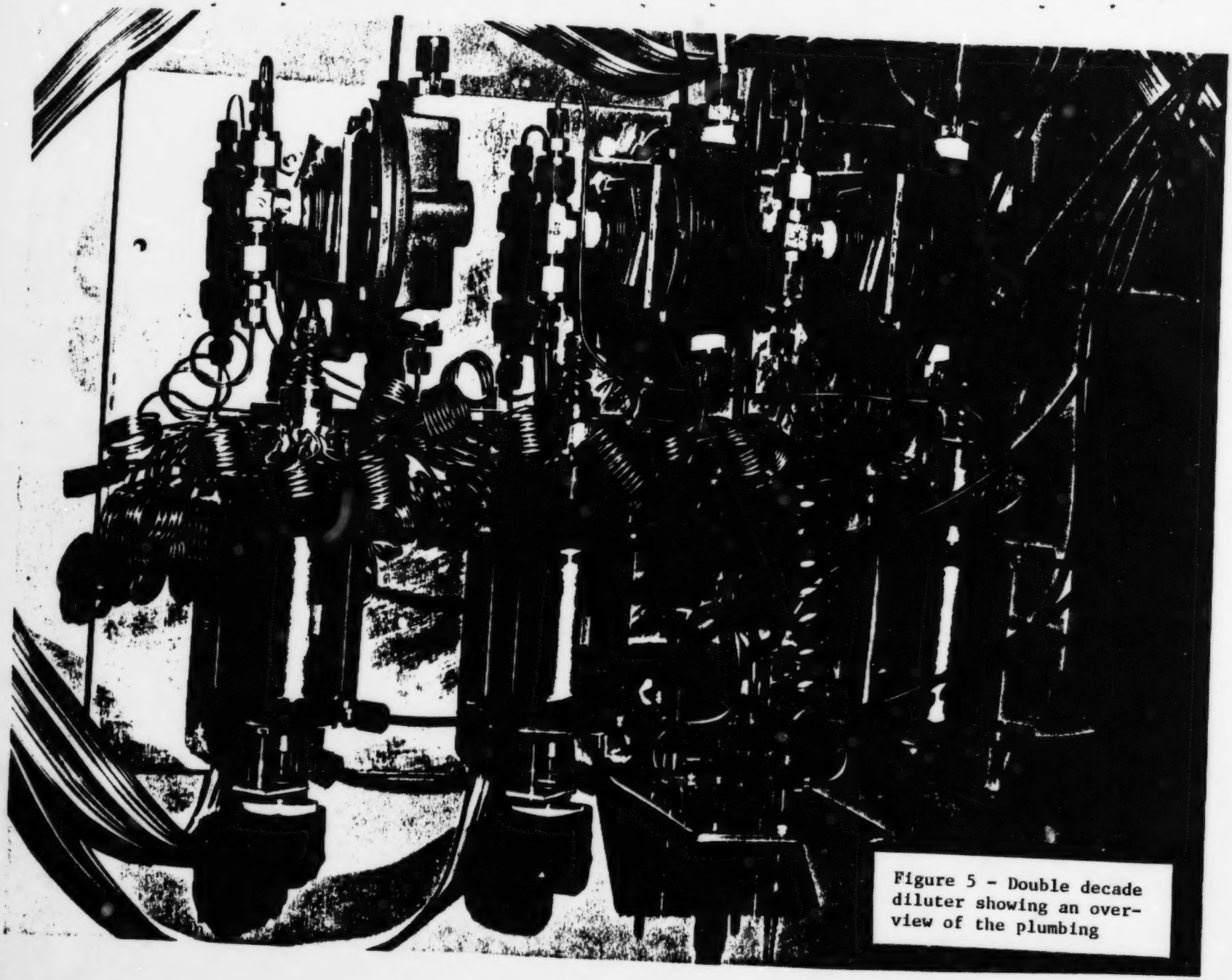


Figure 5 - Double decade diluter showing an overview of the plumbing

FLOW MEASUREMENT

The gas flows were measured using soap bubble flowmeters. The soap bubble flowmeter is a primary standard device that gives gas flows at ambient temperature and pressure. A digital soap bubble flowmeter with a range of 1 to 500 ccm would be the most appropriate device to use with the double decade diluter. A daily record of gas flows can easily be kept using this instrument. Appendix A contains a short basic program for calculating concentrations from gas flows. The program only prompts for the standard concentration and the zero air flow at the beginning. Results are given in parts per billion for the various standard flows entered.

TUBING TIPS

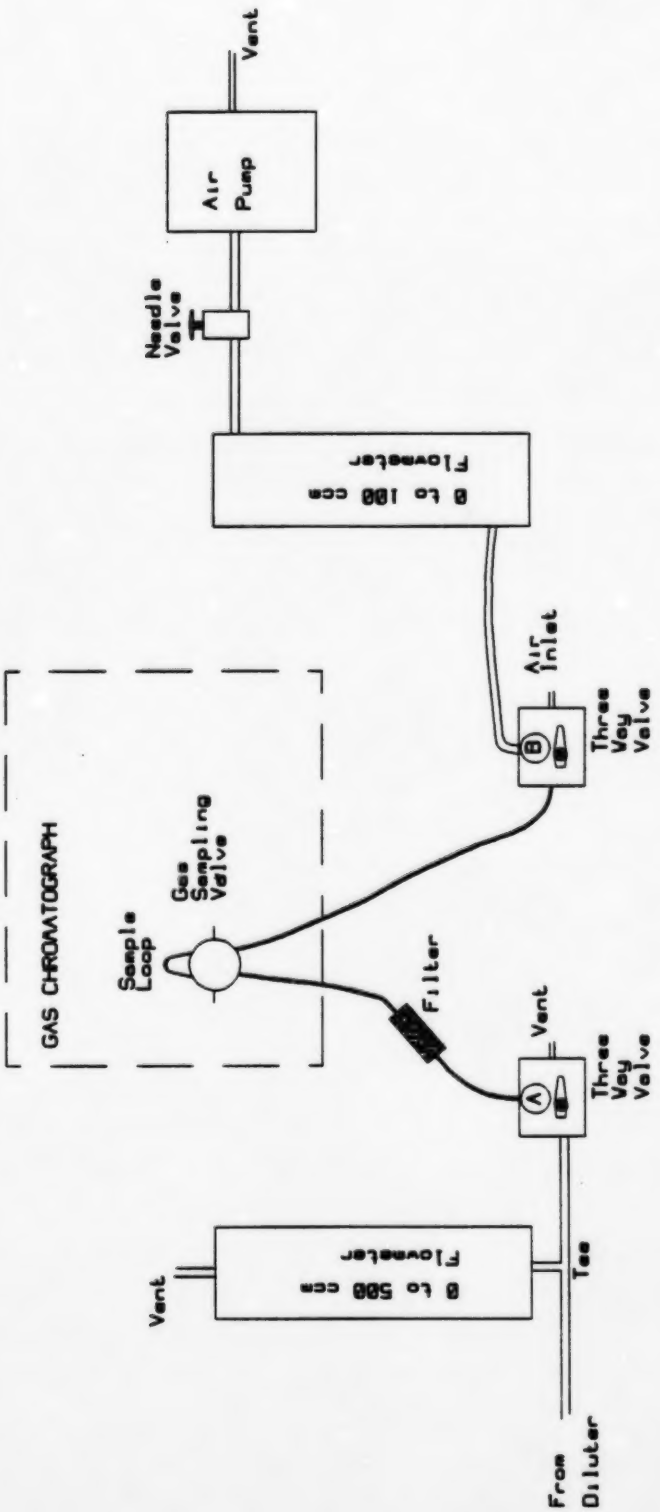
A 1.0 mm (0.04") I.D. by 1.6 mm (1/16") O.D. tubing was used to connect the standard flow controllers to the air actuated switching valve. The same tubing was also used to connect the 16-position valves to the differential pressure regulators. A 3.2 mm (1/8") O.D. tubing was used in the flowpath from the zero air flow controller to the manual switching valve and from the manual switching valve to the mixing tee. The author suggests using a "Terry Tool" tubing cutter on the SS capillary tubing unless the reader has an electronic discharge machine for the job. The "Terry Tool" is available from chromatographic supply houses.

SAMPLE INJECTION

Narrow bore capillary tubing is normally used on a modern gas chromatograph to carry a gas sample from outside the instrument to a loop on a gas sampling valve. Although this permits the analysis of very small samples, problems arise when the sample loop must be filled from a pressurized cylinder. Figure 6 shows how to fill the sample loop with a gas mixture prepared by the double decade diluter.

The gas flow from the diluter will be from 250 to 500 ccm. Most of this is vented through the 0 to 500 ccm flowmeter. A small air pump is regulated by the needle valve to draw from 50 to 100 ccm through the 0 to 100 ccm flowmeter. Valves A and B direct part of the gas mixture from the diluter through the gas sampling valve to the 0 to 100 ccm flowmeter. When the sample loop has been flushed, Valve B is switched directing room air to the 0 to 100 ccm flowmeter and closing the exit from the gas sampling valve. Shortly thereafter, Valve A is switched allowing the gas mixture within the

Figure 6 - Flushing a Gas Sampling Valve



sample loop to equilibrate to atmospheric pressure. The gas sampling valve is then switched injecting the gas mixture onto the chromatographic column.

The vent port on Valve A may also be used for flushing the sample loop with unknown gas samples.

CONCLUSIONS

The double decade diluter is an excellent tool for preparing 32 standard gas mixtures from a cylinder of zero air and two primary standard gas mixtures. The flowrates used to prepare the standard gas mixtures may be accurately measured using soap bubble flowmeters. Variations in barometric pressure should have a minimal effect on the gas mixtures produced by the diluter.

This technique may be useful in the construction of other gas calibrators. For example, a 6-point calibration unit could be made to test the response of combustible gas meters in the lower explosive range. This would require two differential pressure regulators and a 6-position valve. The mixture selection valve could be a simple manual valve for occasional lab or field use. If a large number of meters need to be tested on a regular basis, the valve can be microprocessor controlled to automate the procedure.

REFERENCES

1. Kennedy, D.J. "A rapid sequential tracer gas analyzer suitable for use in an underground environment"; Division Report ERP/CRL 86-70(TR); CANMET, Energy, Mines and Resources Canada; 1986.
2. "Bulletin on Multiposition Valves"; Valco Instruments Co. Inc., Houston, Texas.
3. "Bulletin on Switching Valve Applications"; Valco Instruments Co. Inc., Houston, Texas.

APPENDIX A

A PROGRAM TO CALCULATE GAS MIXTURE CONCENTRATIONS

```
5    PRINT "(Press control+break to exit)"
10   INPUT "air flow (cc/min)=";A
20   INPUT "standard concentration (ppb)=";S
30   INPUT "standard flow (cc/min)=";X
40   C=X/(X+A)*S
50   PRINT "concentration (ppb)=";C
60   PRINT "------------------------------"
70   GOTO 30
```